

AMENDMENTS TO THE CLAIMS

This listing of claims will replace all prior versions, and listings, of claims in the application.

Listing of Claims:

1-22 (Canceled)

23. (New) A process for the preparation of "first-generation" random microgels comprising a step of controlled radical polymerization of a composition comprising at least one monoethylenically unsaturated monomer, at least one polyethylenically unsaturated monomer, a source of free radicals, and a control agent.

24. (New) The process as claimed in claim 23, wherein the monoethylenically unsaturated monomer is:

styrene derivatives,

carboxylic acid vinyl esters,

vinyl halides, vinylidene halides,

unsaturated ethylenic monocarboxylic acids, unsaturated ethylenic dicarboxylic acids, the monoalkyl esters thereof with alkanols having 1 to 4 carbon atoms, optionally N-substituted,

amides of unsaturated carboxylic acids,

ethylenic monomers having a sulfonic acid group, an alkali metal or ammonium salts thereof,

amides of vinylamine,

unsaturated ethylenic monomers having a secondary, tertiary or quaternary amino

group or a heterocyclic group having nitrogen, aminoalkyl (meth)acrylates, aminoalkyl(meth)acrylamides, zwitterionic monomers, (meth)acrylic esters, vinyl nitriles, monomers having at least one boronate functional group or a precursor thereof, phosphonates monomers comprising, N-methacrylamidomethylphosphonic acid ester derivatives, phosphate monomers, monomers having a –C-O-P- sequence in comparison with the –C-P- sequence of the phosphonates, and monomers carrying an alkoxy silane group selected from the group consisting of trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, trimethoxysilylpropyl acrylate,

triethoxysilylpropyl acrylate and tributoxysilylpropyl acrylate.

25. (New) The process as claimed in claim 24, wherein the monoethylenically unsaturated monomer is:

α -methylstyrene, vinyltoluene,

vinyl acetate, vinyl Versatate®, vinyl propionate,

acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid,

acrylamide, methacrylamide, N-methylolacrylamide, N-methylolmethacrylamide,

N-alkylacrylamides,

vinylsulfonic acid, vinylbenzenesulfonic acid, α -acrylamidomethylpropanesulfonic acid, 2-sulfoethylene methacrylate,

vinylformamide, vinylacetamide, N-vinylpyrrolidone, N-vinylcaprolactam,

vinylpyridine, vinylimidazole, dimethylaminoethyl acrylate, dimethylaminoethyl

methacrylate, di(tert-butyl)aminoethyl acrylate, di(tert-butyl)aminoethyl methacrylate,

dimethylaminomethylacrylamide, dimethylaminomethylmethacrylamide,

sulfopropyl(dimethyl)aminopropyl acrylate,

glycidyl acrylate, glycidyl methacrylate,

vinyl nitriles,

acryloylbenzeneboronic acid, methacryloylbenzeneboronic acid, 4-vinylbenzene-

boronic acid, 3-acrylamidophenylboronic acid, 3-methacrylamidophenylboronic acid,

alone or as mixtures, or in the form of salts,

n-propyl ester of N-methacrylamidomethylphosphonic acid, methyl ester of

N-methacrylamidomethylphosphonic acid, ethyl ester of

N-methacrylamidomethylphosphonic acid, n-butyl ester of
N-methacrylamidomethylphosphonic acid, isopropyl ester of
N-methacrylamidomethylphosphonic acid, N-methacrylamidomethylphosphonic
diacid; N-methacrylamidoethylphosphonic acid dimethyl ester, N-methacrylamido-
ethylphosphonic acid di(2-butyl-3,3-dimethyl) ester,
N-methacrylamidoethylphosphonic diacid , N-acrylamidomethylphosphonic acid
dimethyl ester, N-acrylamidomethylphosphonic acid diethyl ester, bis(2-chloropropyl)
N-acrylamidomethylphosphonate, (N-acrylamidomethylphosphonic acid, di(n-propyl)
vinylbenzylphosphonate dialkyl ester, di(isopropyl) vinylbenzylphosphonate dialkyl
ester, diethyl vinylbenzylphosphonate dialkyl ester, dimethyl vinylbenzylphosphonate
dialkyl ester, di(2-butyl-3,3-dimethyl) vinylbenzylphosphonate dialkyl ester, di(t-butyl)
vinylbenzylphosphonate dialkyl ester, vinylbenzylphosphonic diacid, diethyl 2-(4-
vinylphenyl)ethanephosphonate, 2-(acryloyloxy)ethylphosphonic acid dimethyl ester,
2-(methacryloyloxy)ethylphosphonic acid dimethyl ester, 2-(methacryloyloxy)methyl-
phosphonic acid diethyl ester, 2-(methacryloyloxy)methylphosphonic acid dimethyl
ester, 2-(methacryloyloxy)propylphosphonic acid dimethyl ester, 2-
(acryloyloxy)methylphosphonic acid diisopropyl ester, 2-(acryloyloxy)ethylphosphonic
acid diethyl ester, 2-(methacryloyloxy)ethylphosphonic acid (RN 80730-17-2), 2-
(methacryloyloxy)methylphosphonic acid, 2-(methacryloyloxy)propylphosphonic acid,
2-(acryloyloxy)propylphosphonic acid, 2-(acryloyloxy)ethylphosphonic acid;
vinylphosphonic acid, optionally substituted by cyano, phenyl, ester or acetate groups,
vinylidenephosphonic acid the sodium salt thereof, the isopropyl ester thereof, or

bis(2-chloroethyl)vinylphosphonate.

26. (New) The process as claimed in claim 24, wherein the monoethylenically unsaturated monomer is a styrene monomer, vinyl ester, neutral or charged hydrophilic acrylate, hydrophobic acrylate, neutral or charged hydrophilic methacrylate, hydrophobic methacrylate, hydrophilic or hydrophobic acrylamido derivatives, neutral or charged acrylamido derivatives, hydrophilic or hydrophobic methacrylamido derivatives, or neutral or charged methacrylamido derivatives.
27. (New) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomer is an organic compound reactive by the radical route comprising at least two ethylenic unsaturations and at most 10 ethylenic unsaturations.
28. (New) The process as claimed in claim 27, wherein the polyethylenically unsaturated monomer is an acrylic, methacrylic, acrylamido, methacrylamido, vinyl ester, vinyl ether, diene, styrene, α -methylstyrene or allyl derivative.
29. (New) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomer further bears one or more functional groups other than ethylenic unsaturations selected from the group consisting of hydroxyl, carboxyl, ester, amide, amino, substituted amino, mercapto, silane, epoxy and halo functional groups.
30. (New) The process as claimed in any one of claims 1 to 6, wherein the polyethylenically unsaturated monomer is divinylbenzene, vinyl methacrylate, methacrylic acid anhydride, allyl methacrylate, ethylene glycol dimethacrylate, phenylene dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol 200

dimethacrylate, polyethylene glycol 400 dimethacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, 1,12-dodecanediol dimethacrylate, 1,3-glycerol dimethacrylate, diurethane dimethacrylate or trimethylolpropane trimethacrylate; vinyl acrylate, bisphenol A epoxy diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polyethylene glycol 600 diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol ethoxylate diacrylate, butanediol diacrylate, hexanediol diacrylate, aliphatic urethane diacrylate, trimethylolpropane triacrylate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane propoxylate triacrylate, glycerol propoxylate triacrylate, aliphatic urethane triacrylate, trimethylolpropane tetraacrylate or dipentaerythritol pentaacrylate; vinyl crotonate, diethylene glycol divinyl ether, 1,4-butanediol divinyl ether or triethylene glycol divinyl ether; diallyl phthalate, diallyldimethylammonium chloride, diallyl maleate, sodium diallyloxyacetate, diallylphenylphosphine, diallyl pyrocarbonate, diallyl succinate, N,N'-diallyltartardiamide, N,N-diallyl-2,2,2-trifluoroacetamide, the allyl ester of diallyloxyacetic acid, 1,3-diallylurea, triallylamine, triallyl trimesate, triallyl cyanurate, triallyl trimellitate or 1,3,5-triallyltriazine-2,4,6(1H,3H,5H)-trione; N,N'-methylenebisacrylamide, N,N'-methylenebismethacrylamide, glyoxalbisacrylamide or diacrylamidoacetic acid; divinylbenzene and 1,3-diisopropenylbenzene; butadiene, chloroprene or isoprene.

31. (New) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomer is N,N'-methylenebisacrylamide, divinylbenzene, ethylene

glycol diacrylate or trimethylolpropane triacrylate.

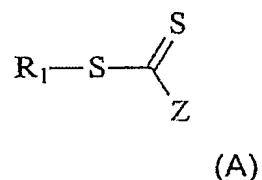
32. (New) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomers with respect to the monoethylenically unsaturated monomers are in a molar fraction of between 0.001 and 1.

33. (New) The process as claimed in claim 32, wherein the molar fraction of polyethylenically unsaturated monomers with respect to the monoethylenically unsaturated monomers is between 0.01 and 1.

34. (New) The process as claimed polyethylenically, wherein the controlled radical polymerization is carried out according to a Atom Transfer Radical Polymerization (ATRP) process or by a reversible transfer by addition-fragmentation of thiocarbonylthio compounds process.

35. (New) The process as claimed in claim 34, wherein the controlled radical polymerization is carried out according to a reversible transfer by addition- fragmentation of thiocarbonylthio compounds process.

36. (New) The process as claimed in claim 35, wherein the thiocarbonylthio compounds are compounds of following formula (A):



wherein:

Z represents:

a hydrogen atom,

a chlorine atom,

an optionally substituted alkyl radical or an optionally substituted aryl radical,

an optionally substituted heterocycle,

an optionally substituted alkylthio radical,

an optionally substituted arylthio radical,

an optionally substituted alkoxy radical,

an optionally substituted aryloxy radical,

an optionally substituted amino radical,

an optionally substituted hydrazine radical,

an optionally substituted alkoxycarbonyl radical,

an optionally substituted aryloxycarbonyl radical,

a carboxyl or optionally substituted acyloxy radical,

an optionally substituted aroyloxy radical,

an optionally substituted carbamoyl radical,

a cyano radical,

a dialkyl- or diaryl-phosphonato radical,

a dialkyl-phosphinato or diaryl-phosphinato radical, or

a polymer chain, and

R₁ represents:

an optionally substituted alkyl, acyl, aryl, aralkyl, alkenyl or alkynyl group,

an optionally substituted, aromatic, saturated or unsaturated, carbon ring or

heterocycle, or

a polymer chain.

36. (New) The process as claimed in claim 34, wherein the thiocarbonylthio compounds are xanthate, dithiocarbamate or dithioester compounds carrying a single functional group of formula –S(C=S)-.

37. (New) The process as claimed in claim 36, wherein the compounds are xanthates.

38. (New) A process for the preparation of “second-generation” random microgels, comprising the steps of:

- 1) preparing a first-generation microgel according to a process as defined in claim 23, and
- 2) adding at least one mono- or polyethylenically unsaturated monomer to the microgel obtained in stage 1) in the presence of an activator.

39. (New) A process for the preparation of “nth-generation” random microgels, n being an integer between 3 and 50, comprising the steps of:

- 1) preparing a (n-1)th-generation microgel as defined in claim 38, and
- 2) adding at least one mono- or polyethylenically unsaturated monomer to the microgel obtained in step n-1 in the presence of an activator.

40. (New) The process as claimed in claim 38, wherein the activator is a source of free radicals.

41. (New) The process as claimed in claim 38, wherein the monomer(s) used in step 2 is or are (a) monoethylenically unsaturated monomer(s) in order to obtain a star-shaped polymer.

42. (New) The process as claimed in claim 39, wherein the monomer(s) used in step n is or are (a) monoethylenically unsaturated monomer(s) in order to obtain a star-shaped polymer.

43. (New) The process as claimed in claim 42, wherein the star-shaped polymer exhibits (1) a central portion in the form of a first-generation microgel based on a crosslinked polymer resulting from the polymerization of the mono- and polyethylenically unsaturated monomers and (2) arms composed of the monoethylenically unsaturated monomers only added starting from step 2 and comprising, at their end, an active part of the control agent (-S(C=S)- functional group), in the case of a controlled radical polymerization process of reversible transfer by addition-fragmentation of thiocarbonylthio compounds type, or the halogen or pseudohalogen part, in the case of a controlled radical polymerization ATRP process .

44. (New) The process as claimed in claim 43, wherein the active part of the control agent (-S(C=S)- functional group) is substituted in all or part by a hydrogen atom or a thiol functional group.